

PREPARATION OF FISCHER-TROPSCH CATALYSTS FROM COBALT/IRON HYDROTALCITES

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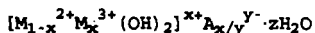
ABSTRACT

Compounds with the hydrotalcite structure ("hydrotalcites") have properties that make them attractive as precursors for Fischer-Tropsch catalysts. A series of single-phase hydrotalcites with cobalt/iron ratios ranging from 3/1 to 1/3 have been synthesized. Mixed cobalt/iron oxides have been prepared from these hydrotalcites by controlled thermal decomposition. Thermal decomposition typically results in either a single mixed metal oxide with a spinel structure or a mixture of oxides with the spinel structure. The BET surface areas of the spinel samples have been found to be as high as about 150 m²/g.

INTRODUCTION

Mixed metal oxides are important in many catalytic applications, both as catalysts and supports. The precursors used in the syntheses of mixed metal oxides are known to influence the physical and chemical characteristics of the resulting mixed metal oxides. Precursors commonly used for the preparation of these oxides include mixed metal hydroxides and carbonates coprecipitated from basic solution. Materials with a hydrotalcite-like structure, commonly referred to as hydrotalcites after one of the best known minerals of this structural group, have received much attention recently as precursors for catalytic applications. Examples include catalysts for methanol synthesis containing Cu, Zn, Cr, and Al (1,2,3) and catalysts for Fischer-Tropsch (FT) synthesis containing Co, Cu, Zn, and Cr (4).

Hydrotalcites have a layered structure similar to clays. The structure consists of stacks of brucite-like metal hydroxide sheets in which substitution of trivalent metal cations for divalent metal cations within the sheets results in a net positive charge. The positive charge is balanced in the structure by hydrated anions between the sheets. A generalized formula for hydrotalcite-like compounds can be written as:



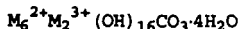
where M²⁺ and M³⁺ can be a variety of metals with appropriate ionic radii. The charge compensating anion is also variable with the ionic radius of the charge compensating anion being of only minor importance because the layer separation can adjust to accommodate size differences. Examples are:

M²⁺ = Mg, Ni, Zn, Co, Fe, Cu, etc.

M³⁺ = Al, Cr, Fe, etc.

A^{y-} = CO₃, OH, SO₄, CrO₄, V₁₀O₂₈, etc.

There are many naturally occurring minerals having this structure. These minerals typically have the ideal stoichiometry:



Compounds with the hydrotalcite structure have several characteristics that make them valuable as precursors for Fischer-Tropsch catalysts. Among these is the ability of the structure to accommodate a variety of potentially useful transition metals in a single lattice and the ability to control the synthesis conditions to yield a high surface area material upon decomposition to a spinel phase. Furthermore, Co-containing and Fe-containing spinel phases have shown good activity and selectivity for FT synthesis and, when judiciously prepared and pretreated, have the potential for the physical stability required of a slurry FT catalyst.

The purpose of this research is to investigate the potential of hydrotalcites as precursors for the preparation of slurry Co/Fe Fischer-Tropsch catalysts. We report results from the initial phase of this work, the preparation of Co/Fe hydrotalcite samples and their thermal decomposition to spinel phases of intermediate-

to-high surface area. The emphasis of future publications will shift to modifications of the precipitation and decomposition procedures described here, the development of suitable pretreatment procedures, and catalytic tests of FT synthesis activity in a fixed bed micro-reactor and a slurry autoclave.

EXPERIMENTAL

The hydrotalcites in this study were prepared by a precipitation in base of the appropriate metal salts. The specific conditions used for the syntheses were varied to yield single-phase, well-crystallized hydrotalcites when possible. An aqueous solution of metal salts was prepared that contained the required ratio of metals for the target hydrotalcite, typically with a total metal concentration of about 0.5 M. The metal salt solution was added dropwise to an aqueous base which typically had an initial concentration of about 1 M. Concentrations were varied for some experiments. Potassium bases were used in most experiments. Potassium is typically used to promote iron F-T catalysts and additional potassium will be impregnated in many of these spinel samples before their use as catalysts. Thus, trace amounts of potassium retained in a hydrotalcite precursor are less likely to affect the behavior of the catalyst than are trace amounts of sodium from sodium bases. Additions were usually done at 25°C with magnetic stirring. The pH was monitored during the syntheses. Usually, at the end of the addition the temperature of the slurry was increased to about 60°C. The slurry was aged, typically for 18 hours, at elevated temperature to promote hydrotalcite formation. After the aging period the product was isolated by filtration, washed and dried at 50°C. Hydrotalcites were thermally decomposed in air at various temperatures between 125 and 1000°C, usually for 2.5 hours, to determine what mixed metal oxide(s) would be formed.

The phases resulting from the hydrotalcite syntheses and the thermal decompositions were determined by means of x-ray diffraction (XRD). Morphologies of these materials were studied with scanning electron microscopy (SEM). Surface areas of the mixed oxides were measured by application of the BET method to N₂ physisorption isotherms. The reduction characteristics of the mixed metal oxides were investigated by means of temperature programmed reduction (TPR) with 10% H₂ in argon, 10% CO in helium, or 5% H₂ / 5% CO in argon. The TPR studies were done using an Altamira Instruments AMI-1 unit with an Ametek mass spectrometer for gas analysis.

RESULTS AND DISCUSSION

A stepwise strategy was used to develop the hydrotalcite syntheses. First, the hydrotalcite compositional range attainable for Co (II) with Fe (III) was determined. Then a method for the addition of Cu (II) to the crystal lattice was tested. Finally, the use of Fe (II) to increase the iron content of the hydrotalcite lattice was investigated.

Cobalt (II) nitrate and iron (III) nitrate were used as starting materials for the first part of the synthesis study. Potassium bicarbonate solution at an initial concentration of 1.25 M was used as the base. Co (II) to Fe (III) atom ratios ranging from 4/1 to 1/3 were attempted in this series of experiments. The results are shown in Table 1. With this method well-crystallized, single-phase hydrotalcites could be prepared with Co (II) to Fe (III) atom ratios from 3/1 to 1/1. At lower cobalt contents some poorly-crystallized iron (III) hydroxide was produced along with hydrotalcite and, at higher cobalt contents, some cobalt carbonate was produced. The starting pH for a synthesis was about 8. During the addition of metal salt solution, the pH typically dropped below 7 and a pinkish-tan slurry formed. As the slurry was aged and heated to 60°C, the pH rose to around 9 accompanied by a change in color to a darker reddish-brown, usually indicating formation of the hydrotalcite.

Copper (II) addition to the hydrotalcite lattice was initially attempted by substituting copper (II) nitrate for part of the cobalt (II) nitrate still using the same synthesis method. (Copper is frequently added to precipitated iron catalysts to facilitate reduction.) The ratio used was 1 Cu (II) / 2 Co (II) / 2 Fe (III). The copper loading used was much higher than typical for Fischer-Tropsch promotion. This high copper concentration was used so that

any undesired phases produced during the synthesis could be detected and identified by XRD. The initial synthesis attempt resulted in primarily hydrotalcite with a trace of malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$. Lowering the base concentration to 1.0 M avoided the malachite contamination resulting in single phase hydrotalcite. This result showed that Cu (II) could be introduced into the Co/Fe hydrotalcite lattice.

A number of experiments were conducted in an attempt to increase the iron content of the hydrotalcite lattice. Table 2 outlines several of the more successful experiments and the resulting compounds. In all experiments in this series metal chloride salts were used. Several of the syntheses were based on the work reported by Uzunova et al. (5). The M^{3+} required for a stable hydrotalcite lattice was provided by the oxidation of some of the Fe (II) to Fe (III) through contact with atmospheric oxygen during the synthesis. The result of this set of experiments was the extension of the hydrotalcite cobalt to iron ratio to 1/3. Work is continuing to increase the iron content to higher levels.

The thermal decomposition behavior of several Co/Fe hydrotalcites were examined. The most extensive studies of decomposition behavior was done for an intermediate composition hydrotalcite, an atom ratio of 2Co to 1Fe, which was decomposed in air at temperatures between 125 and 1000°C. The samples were heated quickly by placing them in a muffle furnace that was already at the desired decomposition temperature and holding them at temperature for 2.5 hours. The results are shown in Table 3. It was found that a spinel phase, referred to as spinel A, was the only crystalline compound present following decomposition at temperatures of 200 to 600°C. Decomposition at 700°C produced a second spinel, spinel B, which was the dominant phase after decomposition at 800°C. Decomposition at 900°C yielded only spinel B, and decomposition above 1000°C began to decompose spinel B to cobalt oxides in addition. The surface areas for these samples were found to drop from 153 to 18 m^2/g . This loss of surface area was probably due primarily to a loss of internal particle porosity because no evidence for sintering was apparent in SEM. Hydrotalcites with other Co to Fe ratios were found to show similar behavior. However, for some high iron hydrotalcites two spinels were always present after decomposition. It was also found that the rate of decomposition at a given temperature influenced the spinels formed.

Preliminary TPR studies were done on a 2Co/1Fe sample decomposed at 600°C. In 10% CO/He, reduction proceeded rapidly above 300°C as reflected by the large mass spectrum peaks at $m/z=28$ and 44. The consumption of CO continued to the end-point of the temperature scan, 450°C. Much of the CO consumption at higher temperatures is likely due to carbon deposition from the Boudouard reaction. In contrast, reduction in H_2 , the typical reductant for Co-rich samples, was less favorable. A TPR in 10% H_2/Ar showed less reduction at 300°C, with reduction rates peaking at about 400°C. In both experiments, the samples were cooled to room temperature in inert gas flow after reaching the 450°C end point of the TPR. In both cases, the predominant solid phase detected by XRD was a cubic phase isostructural with $\alpha\text{-Fe}$. In the case of the CO-reduced sample, a small amount of an additional unidentified phase was also present.

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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Table 1. Results of Co (II)/Fe (III) hydrotalcite preparations using metal nitrates.

<u>Co (II) to Fe (III)</u>	<u>Resulting Phases</u>
4/1.	HTC + trace CoCO_3 + trace unidentified
3/1	HTC + trace CoCO_3
2/1	HTC
1/1	HTC
1/2	HTC + minor $\text{Fe}(\text{OH})_3$
1/3	HTC + $\text{Fe}(\text{OH})_3$

HTC = hydrotalcite

Table 2. Use of Fe (II) to increase iron content of hydrotalcite prepared using metal chlorides.

<u>Co (II)</u>	<u>Fe (II)</u>	<u>Base</u>	<u>Start pH</u>	<u>Result</u>
1	3	KHCO_3	8.0	HTC + trace $\text{Fe}(\text{OH})_3$
1	3	$\text{KHCO}_3 + \text{K}_2\text{CO}_3$	8.9	Goethite + CoCO_3
1	2	$\text{KOH} + \text{K}_2\text{CO}_3$	12.8	HTC
1	3	$\text{KOH} + \text{K}_2\text{CO}_3$	12.8	HTC

HTC = hydrotalcite

Table 3. Thermal decomposition of 2Co/1Fe hydrotalcite.

<u>Temperature °C</u>	<u>Phase</u>	<u>Surface area m^2/g</u>
50	HTC	-
125	HTC + amorph.	-
200	Spinel A	-
300	Spinel A	153
400	Spinel A	95
500	Spinel A	57
600	Spinel A	29
700	Spinel A + B	18
800	Spinel A + B	-
900	Spinel B	-
1000	Spinel B + $\text{CoO} + \text{Co}_3\text{O}_4$	-